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PRIMARY THERMAL UPGRADING OF

RESIDUA TO TRANSPORTATION FUELS

Final Report

by

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1. SUMMARY

Vacuum Tower Bottoms (VTB) derived from Interprovincial Pipeline crude (IPL), Lloydminster heavy oil (LL) and Athabasca bitumen (A) were thermally upgraded at high temperatures in the absence of external hydrogen. Both the bench scale (ca 150 g of feed) and microscale (1 - 5 g of feed) tests were performed. Effects of processing conditions, steam injection and addition of solid substrates on the yield and quality of the products were evaluated. The bench tests employing either steam injection or solid substrates as well as microscale tests were carried out at 510°C. The solid additives comprised iron ore, sand, vanadate slag and metalloporphines.

The steam injection and increasing temperature affected boiling point distribution in total liquid product. The iron ore and slag increased gas yield, while nickel and vanadium porphines decreased total liquid product yield. In general, it was found that the microscale test was more efficient than the bench scale test for monitoring of the product yields.

The differences in coke and liquid product characteristics from the VTB of A, LL and IPL are reported. The mass spectrometric analyses revealed the superiority of gas oil derived from the VTB of IPL for FCCU operations, while coke of the same origin, characterized by thermogravimetric analysis, was better quality than those of A and LL.

2. INTRODUCTION

2.1 OBJECTIVE

The overall objective of this project was to investigate and compare yields and characteristics of products derived from thermally upgraded VTBs of conventional crude, heavy oil and bitumen.

The specific objectives were as follows:

- to assess the effects of steam injection and solid additives on product yields;
- to obtain information on the quality of liquid product;
- to evaluate the effect of feed type and processing conditions on the characteristics of coke;
- to evaluate the feasibility of performing microscale coking tests for determining/monitoring product yields.

2.2 BACKGROUND

Several primary thermal upgrading processes are applicable to heavy ends. Processes such as coking (1) and visbreaking (2) offer effective upgrading of residual oil in the absence of added hydrogen. Viable alternative is provided for residue demetalization and desulfurization by contacting a porous refractory oxide with residuum at coking temperatures (3,4).

The thermal cracking technology has considerably advanced in the past two decades; however, the key process variables and parameters of feedstock quality, which influence conversion yields, are only slightly covered in the literature (5,6).

Although thermal cracking has become an obsolete processing route for producing transportation fuels, three thermal cracking process types are in common use. The most widely used is "steam cracking", in which straight-run naphtha is converted to a range of low molecular olefins. The two other forms of thermal cracking are "visbreaking" and "coking". Both are used to convert residual oils, but whereas visbreaking is carried out under relatively mild

conditions as a means of reducing feedstock viscosity, coking is conducted at high severity to produce distillate oils and coke.

In efforts to maximize light transportation fuel yield, refiners use coking as a primary upgrading process. Coking processes are extreme forms of thermal treatments, in which the ultimate of total extinction of feed is practised, to convert heavy ends, such as atmospheric and vacuum residua, tars and pitches into more valuable lighter products. There are two main types of coking processes available; namely, delayed and fluid coking. The latter process, in advanced form, is also known as flexicoking whereby the fluid coke produced is gasified to produce low thermal value gas.

Delayed coking can be described as a semi-continuous process in which the feedstock is pumped to the coker heater where it is heated to coking temperature, which produces partial vaporization and mild cracking. The vapour-liquid mixture then enters the coke drum where the vapor experiences further cracking as it passes through the drum and the liquid experiences successive cracking and polymerization until it is converted to vapor and coke.

Fluid coking is a continuous process. The residue is coked by spraying into a fluidized bed of hot, fine coke particles. The use of a fluid bed permits the coking reactions to be conducted at higher temperatures and with shorter contact times than in delayed coking. These conditions result in lower yields of coke and higher yields of liquid products.

Thermal cracking reactions are believed to proceed through the formation of hydrocarbon free radicals (7). Free radicals are formed by carbon-carbon bond scission, generally towards the center of a hydrocarbon molecule. Unlike the carbonium ions formed in catalytic cracking, free radicals carry no electrical charge. Reactions employing free radicals include:

- hydrogen transfer to form a new hydrocarbon, generally of lower molecular weight and another free radical;

- addition reactions with olefins;

- paraffin formation from the free radicals.

Under severe thermal cracking conditions, carbon-hydrogen bond scission may also occur. An example of this would be the dehydrogenation of an olefin molecule to form a diene. In view of the hydrocarbon reactivity, the ease with which the hydrocarbon types can be thermally cracked decreases in the following order: normal paraffins, iso-paraffins, cycloparaffins, aromatics, aromatic/naphthenic types and polynucleararomatics.

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3. EXPERIMENTAL

3.1 FEEDSTOCKS

The VTBs of IPL crude and Lloydminster heavy oil were supplied by Petro-Canada Clarkson Refinery. Athabasca bitumen, obtained from Syncrude Plant (Hot Water Process), was in-house distilled to yield VTB fraction. Information on the feedstocks employed in the thermal upgrading tests is compiled in Table 1.

3.2 SUMMARY OF THE WORK UNDERTAKEN

Tables 2-6 compile information on the coking tests. The tests performed were as follows:

Test Name/Feed	Variable	Table	No. of Tests
Coking/IPL	3 Temperatures	2	3
Coking/Lloydminster	2 Temperatures	2	3
Coking/Athabasca Bitumen	2 Temperatures	2	4
Steam Injection/IPL	---	3,6	2
Steam Injection/Lloydminster HO	3 Injection Rates	3,6	4
Steam Injection/Athabasca Bitumen	---	3	1
Coking with Iron Ore/ Lloydminster HO	---	4	1
Coking with Iron Ore/ Athabasca Bitumen	---	4	1
Coking with Slag/Lloydminster HO	---	4	1
Coking with Slag/Athabasca Bitumen	---	4	1
Coking with Sand/ Lloydminster HO	2 Feed-Sand Ratios	5,6	4
Coking with Sand/Athabasca Bitumen	2 Feed-Sand Ratios	5,6	3
Coking-Repetition/IPL	---	6	1
Coking-Repetition/Lloydminster	---	6	1
Coking/Model Feed	3 Metal Contents	6	3
	TOTAL NO. OF TESTS		33

The liquid products were analyzed for nitrogen and sulfur contents. The gravity and viscosity of these products were also examined. Selected samples of the liquid products were fractionated and the fractions were analyzed for sulfur, nitrogen and hydrocarbon contents.

Selected coke samples were analyzed for sulfur, nitrogen, carbon and ash contents and characterized by scanning electron microscopy and thermogravimetric methods.

The gas effluent compositions were determined by low resolution mass spectrometry.

In addition, eight microscale coking tests were carried out (Table 7). The yields of products: gases, liquids and coke were individually determined for calculating a complete product yield. The liquid effluents were analyzed for boiling point distribution by gas chromatography, while the gas effluent compositions were determined by mass spectrometry.

3.3 METHODOLOGY

Two methods were adopted for cracking the vacuum tower bottoms to produce the liquids, gases and coke. The first method utilized a 300 cc autoclave and heater as shown in Figure 1. The products from the autoclave test gave sufficient quantities of liquid for further characterization.

The micro tests were carried out using a dynamic system of sample injection of the VTB using an automatic syringe pump. The system is shown in Figure 2. This procedure was quick and used small quantities of VTB while still yielding sufficient quantities of liquids, gases and cokes for mass balance calculation and product characterization studies.

3.3.1 Macroscale Tests

Approximately 150 g of molten VTB was introduced into the autoclave and sealed with a top mounted flange (Figure 1). The autoclave was fitted with steel outage tubing to carry liquids over into a condenser.

The autoclave contained thermocouples to record and control the temperature of the reaction zone.

The autoclave contained gas purge lines, steam injection lines, bursting disk and pressure indicator for safety reasons. VTBs were heated to temperatures of 460°C and higher and the thermally-cracked liquids evolved along with gases.

The liquids were trapped in an impinger mounted in an ice bath while the sour gases were sampled and passed through a wet test meter.

- The autoclave was held at the maximum desired temperature until no more liquid was produced (approximately 1 hour).

- The liquids were weighed to calculate the yield while gas samples were collected and analyzed by mass spectrometry.

- The coke remaining in the autoclave was scraped from the walls and weighed to calculate the percent of coke produced.

- The coke was further extracted with toluene and methylene chloride to remove residual VTB from the cokine using a standard Soxhlet apparatus.

- Water was injected prior to the cracking using a micro pump.

- Nitrogen was used to carry the liquids over and prevent condensing of liquids and plugging of lines.

3.3.2 Coking with Solid Substrates

VTBs were mixed with solid substrates at ratios of 3 to 1 and 6 to 1. The substrates were sand, iron ore and slag.

Approximately 135 g of VTBs were heated and the correct ratio and amount of the above solids were added. The mixture was stirred and introduced into the autoclave. Similarly quantities of nickel and vanadium porphines were added in known amounts to IPL vacuum tower bottoms.

3.3.3 Microscale Tests

Samples of VTB were loaded into 5.0 mL glass syringes, the VTBs were kept liquid in the syringe immobilized in a heated syringe holder.

A small tube furnace was mounted below the syringe. The reactor tube (1.2 x 15 cm) made from stainless steel contained a sample outage tube, and gas purge line. The capillary tubing 3 mm O.D. was used to convey VTB from the syringe to the center of the reactor tube.

Approximately 5.0 g of sample was cracked in the microreactor arrangement. The liquids were collected and weighed in a small impinger while the gases were collected in a 2-litre glass container using displacement of a brine solution as a measure of the gas produced.

The gas collected was subsequently analyzed by mass spectrometry and the coke was recovered from the reactor tube.

The syringe was weighed after the injection was complete to obtain the yield of liquids, coke and gas.

The injection rate was approximately 0.15 g/min.

3.4 SOLID SUBSTRATES

Eleven bench scale cracking tests were carried out in the presence of a solid substrate added in a ratio of 3:1 and 6:1 (oil to solid). The following solids were used:
iron ore (magnetide) from Iron Ore Co. of Canada;
sand separated from Athabasca bitumen (Syncrude Plant, Alberta);
and vanadate slag from smelting process.

Coking of model feeds employed two metalloporphinic additives. These were:
Nickel(II)-meso-tetraphenylporphine and
Vanadium(IV)-meso-tetraphenylporphine. Both reagents were obtained from Morton Thiokol, Danvers, MA, USA.

3.5 CHARACTERIZATION OF LIQUID PRODUCTS FROM CRACKED VTB CRUDES

3.5.1 Sample Preparation

The liquid product yielded from the macro cracking (Vacuum Tower Bottoms) was subsequently distilled using ASTM D1160 methods. The liquid product was fractionated into four fractions: IBP-190°C, 190-290°C, 290-360°C and 360°C+.

3.5.2 Analyses of Fractions

The cracked liquids from IPL, Lloydminster, and Athabasca crudes were characterized using the following analytical test procedures:

a) High resolution mass spectrometric analysis of the 360°C+ fraction
b) Low voltage mass spectrometric analysis of fraction, IBP-190°C
c) Middle distillate mass spectrometric analysis of fractions, 190-290°C and 290-360°C
d) Bromine number on all samples except the 360°C+ fraction using Electrometric Titration as outlined in ASTM D1159
e) Densities using a Parr Densitometer as outlined in ASTM D4052
f) Viscosities were recorded on all samples except the IBP-190°C fraction using ASTM D445 and a standard Oswald Viscometer
g) Sulfur content using X-ray Fluorescence spectrometry
h) Nitrogen content measuring chemiluminescence of nitric oxide.

a) High Resolution Mass Spectrometry (HRMS) of Gas Oils

The mass spectrometric analyses on selected extracts were performed on an AEI MS-902 high resolution mass spectrometer from Kratos, Manchester, England. The mass spectrometer was operated at a dynamic resolution of 10 000 minimum and scans were collected at about 3 minutes per mass decade. The ion source operated at 250°C in the EI-mode at an electron beam energy level of 57 eV nominal. Several spectral scans with a constant total ion current and consistent number of peaks were used for the computations and interpretations.

The atomic compositions for all observed mass peaks were computed on a Kratos DS-55 datasystem/DG Nova-3 computer. Possible atomic compositional data for molecules containing up to two heteroatoms

from S, O and N were permitted in the computations. Subsequent data reductions and manipulations used special in-house custom software.

b) Naphthas by Mass Spectrometry

The analysis was based on the summations of the intensities of characteristic fragment ions to determine the concentration of each hydrocarbon type. The depentanized sample (or the original sample if not depentanized) was admitted to the mass spectrometer by means of a capillary dipper or high pressure liquid sampling valve. The mass spectral contributions of the C_3-C_5 hydrocarbons (determined by gas chromatography) were removed from the sample spectrum. Then Carbon Number distributions for the group types were computed from the intensities of their molecular ions; these distributions in turn were used to assemble an appropriate calibration matrix. Sample composition, expressed in liquid volume %, was calculated from the resulting matrix by computing an inverse.

c) Distillates by Mass Spectrometry

The analyses were performed using a method similar to that described in the publication by C.J. Robinson in Anal. Chem. in 1971.

d) Bromine Number

A sample of distillate was dissolved in a solution consisting of glacial acetic acid, chloroform, methanol and sulfuric acid. The sample was titrated electrometrically with a standardized Bromide-Bromate solution using a polarized Platinum Electrode system.

e) Density

Densities on the distillates were measured with a Parr Densitometer using the change in frequency oscillations as a function of the mass of material held in a vibrational field.

f) Kinematic Viscosity

The kinematic viscosity was determined from the calibration constant of the viscometer and the drop time of the liquid.

The viscosities and timing of the drop rate were determined manually at 40°C using a viscometer requiring approximately 200 s. Viscometers used were pre-calibrated and checked with standard oil samples.

Viscosities were determined with an Oswald viscometer supplied by Cannon.

g) Determination of Sulfur Content

A sample of the cracked liquid was irradiated with an X-ray beam. The emitted radiation was measured as a function of the sulfur content. The analyzer used was supplied by Horiba Instruments model SLFA-920.

h) Determination of Nitrogen Content

A sample was injected into a pyrolysis furnace enriched with oxygen. The nitrogen compounds were converted to nitrous oxide and swept by helium gas into a reaction chamber containing ozone.

The reaction between ozone and nitrous oxide produced a chemiluminescent reaction and a corresponding quantity of light proportional to the nitrogen content.

The analysis was carried out using an Antek nitrogen analyzer Model 771 Pyro Reactor and an Antek Model 720 Photomultiplier detection unit.

3.6 GAS ANALYSIS BY MASS SPECTROMETRY

The quantitative analysis of gaseous mixtures for hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, 27 C_1-C_8 hydrocarbons (or hydrocarbon types), air and water was performed.

The molecular species which make up a gaseous mixture were ionized and dissociated by electron bombardment in a mass spectrometer and a mass spectrum was recorded. Water was determined unicomponently from the corrected spectrum and its contribution was removed.

Then 9 C_6-C_8 hydrocarbons were determined by solution of simultaneous equations and their contribution to the spectrum was removed. Finally 21 hydrocarbon and non-condensable gases were determined by solution of simultaneous equations.

3.7 CHARACTERIZATION OF COKE

3.7.1 Thermogravimetric Analysis

The analyses were carried out using thermal analyzer Model 1090 from DuPont Instruments, Wilmington, Delaware. The volatile release profiles were determined monitoring mass loss with increasing temperature under nitrogen, while the determination of the combustion profiles employed air. The combustion data are reported using parameters as follows:

T_o Combustion onset temperature - Defined as the temperature at which the derivative of mass loss curve leaves or crosses the zero line. T_o is therefore the maximum point of mass gain due to oxidation.

T_{xo} Extrapolated combustion, onset temperature - Intersection of tangent drawn at T_o and tangent at point of inflection T_i on combustion mass loss curve.

T_i Tangent at first point of inflection on mass curve.

T_{xc} Temperature of complete combustion - Intersection of tangent drawn at last point of inflection and constant mass.

T_{25}, T_{50}, T_{75}
Temperatures of 25%, 50% and 75% combustion of carbonaceous material (corrected for ash content).

3.7.2 Scanning Electron Microscopy

Selected coke samples from macro- and micro-tests were examined for presence of pores and crevices as well as semi-quantitative analysis for the metal contents and presence of other elements performed. The coke characterization employed JEOL Model JSM-3 5CF Scanning Electron Microscope equipped with X-ray probe.

4. RESULTS AND DISCUSSION

4.1 COKING TESTS

4.1.1 Reference Coking Runs (Bench Scale)

Thermal upgrading runs were carried out on all three feeds, the intent being to evaluate the effect of temperature and feed type on the product yields. The information derived was also used to set test conditions for runs employing either the addition of solid substrate or steam injection.

The highest total liquid product (TLP) yield was observed for IPL residuum, while the VTB of Athabasca bitumen yielded the least amount of the liquid product (Table 2). The yields were found to increase with increasing temperature. Increase in temperature was also responsible for changes in boiling point distribution. At higher temperatures, the VTBs of IPL crude and Lloydminster heavy oil yielded more middle distillate, whereas that of Athabasca bitumen had higher gas oil content. The total liquid product derived from IPL VTB was relatively low in sulfur. In contrast, the liquid effluents of Athabasca bitumen and Lloydminster VTB origin were high in sulfur and its concentrations similar. The nitrogen contents did not differ significantly for the liquid effluents derived from all three feed types.

The coke yield increased in order, IPL, Lloydminster and Athabasca VTB. The first two feeds generated approximately equal amounts of gas. The highest gas yield was observed for Athabasca bitumen VTB at 490°C. The compositional analyses revealed the highest methane - and lowest hydrogen sulfide - contents in gas derived from IPL VTB. The hydrogen sulfide content in gas effluents increased in the same order as coke yields, while the converse occurred for the methane content.

With the above background information, the temperature 510°C was chosen for performing all the other tests.

4.1.2 Coking with Steam Injection

The steam injection had minor effect on the total liquid product yield, while decrease in the amount of coke and gas produced was

observable (Tables 3 and 6). An injection rate as low as 0.06 g/min was sufficient to influence coke and gas yields. The higher the rate, the more coke was produced when upgrading the VTB of LL. The steam also caused changes in distribution of liquid products. The steam treating of the VTBs from IPL and LL led to lower naphtha and distillates content than those obtained by the thermal treatment alone. The gas oil content increased significantly due to the steam presence. The above effects were accompanied by higher sulfur and nitrogen contents of the total liquid product. There was also a trend towards higher specific gravity values for the fractions derived from the VTBs cracked when injecting steam.

4.1.3 Coking with Iron Ore or Slag

The presence of iron ore decreased the extent of coking, while increasing gas yield. The slag addition decreased the total liquid product yield, while significantly increasing conversion into gas. The liquid effluent from the latter tests was found to contain less sulfur and nitrogen species than the effluent from preceding tests.

4.1.4 Coking with Addition of Sand

Inconclusive results were obtained. They are reported in Tables 5 and 6.

4.1.5 Coking with Addition of Metalloporphines

Three tests employing IPL VTB and metalloporphines were carried out (Table 6). In tests 1 and 2 the latter were added into the residuum to increase either its nickel or vanadium content to a level matching that of the VTB of Lloydminster heavy oil. In the third test the amount of the added vanadium compound was doubled. Increase in vanadium or nickel content was found to decrease total liquid product yield. The addition of vanadium porphine also increased gas oil content of the total liquid product.

4.1.6 Microscale Coking Tests

Eight tests were performed (see Table 7) to compare product yield structures with those observed in the autoclave tests. The first three tests with IPL VTB at 0.135 g/min addition rate gave lower liquid yields than those from the macroscale tests.

Tests 4 and 5 led to product yields similar to those reported in Table 2. Shorter residence time and charge increased to 5-6 g resulted in more consistent data. Test 4 involving two successive injections proved to be useful for quick and repetitive determinations of liquid effluent yields. Tests 6, 7 and 8 employing the residuum derived from Lloydminster heavy oil revealed a good match between product yields obtained in both test types. In spite of yield similarities in both test types for IPL and Lloydminster VTBs, different boiling point distributions were observed. IPL VTB cracked in the bench test yielded liquid effluents containing components of lower boiling point than those present in the liquid effluent from the micro-scale test. The reverse occurred for Lloydminster VTB. Typical boiling point distributions are shown in Table 8. These differences in boiling point distribution and corresponding differences in gas content seem to reflect the effect of the residence time on the extent of cracking. IPL VTB was converted more readily into gas in the micro-test apparatus than in the autoclave, while cracking of LL VTB in the former yielded more light liquid, than that in the latter. Therefore, it appears that the applied residence time was sufficient for desirable conversion of LL VTB and too long for IPL VTB (over-cracking). In all the microscale tests gas effluent yields were higher than those reported in Table 2, because of the presence of purging nitrogen. In general, the tests performed proved to be quick and demonstrated the potential for investigating/monitoring coking processes.

4.2 CHARACTERIZATION OF LIQUID PRODUCTS

Selected liquid effluents were fractionated into four cuts: IBP-190°C, 190-290°C, 290-360°C and 360°C+. The cuts were tested for bromine number, specific gravity, sulfur content and nitrogen content (Tables 9-11). The distributions of hydrocarbon types, thiophenes and oxygen compounds were determined by means of mass spectrometry (Tables 12-16). The differences in the contents of hydrocarbon and sulfur types are shown in Figures 3-6.

The effects of feed type and processing variables on the fraction characteristics are described below.

4.2.1 Naphthas

Naphthas derived from A VTB and LL VTB had higher sulfur and nitrogen contents than those of IPL VTB. Figure 3 illustrates varying contents of three hydrocarbon types in these three VTB derived naphthas. The monoolefinic content increased in the order as follows: IPL, LL and A. A reverse sequence was observed for the contents of monocycloparaffins and alkylbenzenes.

The injection of steam, when thermally cracking the VTBs of IPL and LL, modified compositions of both naphthas. The dicycloparaffinic and monoolefinic contents decreased due to the presence of steam. Accordingly, both naphthas had lower bromine numbers than those obtained from the reference runs.

4.2.2 Light Distillates

The VTBs of A and LL yielded distillates of high sulfur and nitrogen. The sulfur content of the distillate derived from IPL VTB was low and nonthiophenic. The paraffinic content decreased in the following order: IPL, LL and A. The monoaromatic and thiophenic contents increased in a reversed order (as shown in Figure 4).

The addition of nickel porphine to the IPL VTB resulted in the decreased content of paraffins and increased content of monoaromatics.

4.2.3 Heavy Distillates

The compositional analyses revealed that the heavy distillates derived from IPL VTB had the lowest sulfur content, while contents of nitrogen were similar for all three feed types and not influenced significantly by temperature, solid substrates and steam injection. Figure 5 illustrates compositional differences in hydrocarbon content. The paraffinic content decreased in sequence IPL, LL and A, while monoaromatic, diaromatic and thiophenic contents increased in the reversed sequence.

The injection of steam was found to decrease the paraffinic content and increase the concentrations of cycloparaffins. The addition of nickel porphine also reduced the paraffinic content, while the monoaromatic content increased.

The VTB of Athabasca bitumen cracked in the presence of sand produced a distillate higher in cycloparaffins and lower in di- and tri-aromatics than those from the reference runs.

4.2.4 Gas Oils

The sulfur content of the gas oils derived from the IPL VTB was considerably lower than those from the VTBs of LL and A (Table 9). As can also be seen from Table 9, the nitrogen contents were relatively high (2000 ppm range) and did not reflect their origin. More significant differences were observed by means of mass spectrometric analysis. The saturate content decreased, whereas the contents of the aromatic hydrocarbons and thiophenes increased for feeds in the order of: IPL, LL and A. The mass spectrometric analyses also permitted to assess levels of the precursors (i.e. the combined content of saturates and monoaromatics) for gasoline in FCCU operations. The contents indicated a superiority of gas oil of the IPL VTB origin. The precursor levels, in mass %, were as follows: 83.3 - IPL, 55.1 - LL and 51.9 - A.

The addition of nickel porphine increased the saturate content, while decreasing the content of monoaromatics. The steam injection increased only the content of cycloparaffins, but reduced the contents of paraffins and monoaromatics.

A higher content of cycloparaffins and lower contents of di- and tri-aromatics were observed for the gas oil fraction obtained from cracking VTB of Athabasca bitumen with sand.

4.3 CHARACTERIZATION OF COKE

4.3.1 Thermogravimetric Analysis

Selected samples of coke were analyzed for combustion and volatile release profiles (Tables 17 and 18). The cokes from all three feed types cracked at 510°C gave similar combustion profiles. Coking at 460 and 490°C yielded softer and easier combustible cokes. The steam injection had similar influence as cracking at the lower temperatures. In general, cokes derived from IPL VTB were found to generate less ash, than those from the Lloydminster heavy oil and Athabasca bitumen.

TGA allowed the characterization of cokes obtained from the microscale tests and a comparison of these cokes with those from the macroscale runs. Microscale test cokes derived from the VTBs of IPL and LL gave similar combustion and volatile release profiles. These microscale test cokes, however, had more fixed carbon and generated more volatiles and ash than the cokes from the macroscale tests.

4.3.2 Scanning Electron Microscopy

Ten samples were examined by SEM. The results of the semi-quantitative analysis are listed in Table 19. All ten samples contained the elements S and Si. However, some samples contained one or more other elements (Table 19). The major coke constituents i.e. elements such as carbon, hydrogen and oxygen were not determined (the X-ray probe is not capable of detecting them).

The contents of the detected elements were determined from the 'dot maps' (dispersion characteristics). The analyses revealed that most of the samples were homogeneous. These were coke samples from microscale cracking of IPL VTB and coke derived from coking of its VTB with steam injection. Both cokes showed areas of high concentration of elemental iron.

Finally, all ten samples were air brushed to eliminate fine dust then gold coated for imaging. Photographs were taken of surface and fractured area of magnification of 2000 and 20,000. All samples were similar in structure except Athabasca bitumen coke (test at 490°C). Two photographs are shown in Figure 7 - one represents typical surface while the other more granular type.

5. CONCLUSIONS

The performed thermal upgrading tests provided comparative data on three feed types, which were the VTBs of Interprovincial Pipeline crude, Lloydminster heavy Oil and Athabasca bitumen. The study permitted several conclusions on the effect of the operating conditions, steam injection and addition of solids on the thermal upgrading yields and product characteristics. The conclusions are as follows:

1. The higher the temperature the higher the total liquid product yield. Increase in temperature is also responsible for changes in boiling point distribution. The VTBs of IPL and of A yielded more middle distillate, whereas the VTB of A yielded more gas oil at higher temperature.

2. The steam injection affects boiling point distribution of the total liquid products. Both higher specific gravity values for the fractions of the total liquid product and lower contents of naphtha and distillates were observed. In addition, the compositional characteristics of the fractions were modified in comparison to those from the reference runs.

3. The addition of solids such as iron ore, slag and nickel or vanadium porphine is detrimental to conversion of the residuum to light liquid products. The iron ore and slag increased gas yield, while porphines decreased total liquid product yield. Some changes in compositional characteristics were also observed.

4. The gas oil and coke of the IPL VTB origin are better quality than those derived from A and LL.

5. Due to the speed, convenience and good reproducibility, the microscale test is more efficient and more effective than the bench scale test for monitoring processability of thermally upgraded feedstocks.

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TABLE 1

FEEDSTOCK INSPECTIONS

VTB		I.P.L.	Lloydminster	Athabasca
Sp. Gravity		0.9916	1.0420	1.0599
Viscosity, cSt	100°C	604		
	135°C	110	1191	1476
	150°C	67	576	665
	175°C		206	228
Asphaltene Content, % nC_4 n sols ASTM D3279		10.3	20.8	20.1
Metals, ppm	Fe	12.4	46.2	643
	Ni	17.8	64.4	108
	V	29.8	137	281
Total Sulfur, w/w %		1.25	6.36	6.78
Total Nitrogen, ppm		4500	5301	6223
GCD, °C	IBP	350	340	342
	5%	524	474	453
	10%	546	495	487
	20%	574	532	533
	30%	600	566	572
	42%	634	611	625
Conradson Carbon		13.9	19.9	21.0

TABLE 2

COKING TESTS - REFERENCE RUNS (BENCH SCALE)

VTB	I.P.L.			LLOYDMINSTER			ATHABASCA			
Coking Temperature, °C	460	490	510	460	510		490		510	
Reactor Charge Wt. (g)	157.5	159.3	172.7	152.9	201.7	174.0	145.7	176.9	146.3	135.4
% Light Oils w/w	54.7	65.8	64.8	51.9	57.2	54.2	46.3	45.6	48.8	52.5
% Coke w/w	21.3	16.0	19.0	23.7	29.1	27.7	23.6	26.9	29.2	32.7
% Uncracked VTB w/w	5.3	10.9	7.3	6.4	3.3	7.5	20.1	18.2	7.4	0.7
% Gases w/w	5.5	7.6	7.5	5.0	7.4	8.5	11.9	10.3	8.0	8.0
Material Balance	96.8	100.3	98.6	94.0	97.0	97.9	101.9	101.0	93.4	93.9
Physical Properties Liquid										
Aniline Point	60.6	67.6	65.5	45.8	46.4		40.9		41.8	
Gravity	0.8307	0.8489	0.8403	0.8631	0.8712		0.8508		0.8795	
Viscosity, cSt 40°C	2.42	3.79	3.02	2.65	3.20		1.93		3.16	
Total Sulfur, %	0.55	0.53	0.52	3.35	3.45		3.35		3.71	
Total Nitrogen, ppm	1054	1109	1152	905	924		927		1412	
Fractionation G.C.D.	64.7	65.8	64.8	51.9	54.2		46.0		50.6	
IBP-190°C, % wt	24	18	21	23	21		29		22	
190-290°C, % wt	28	22	25	27	26		34		26	
290-360°C, % wt	27	33	36	24	32		22		21	
360°C+, % wt	21	27	18	26	21		15		31	
Gas Composition, mole%	5.5	7.6	7.5	5.0	7.4	8.5	11.9	10.3	8.0	8.0
H_2	5.0	3.5	5.5	8.8	7.0	6.8	6.5	7.3	8.0	4.6
C_1	46.2	40.0	47.5	41.8	37.4	38.7	28.8	30.9	33.3	28.1
C_2	19.5	18.9	19.6	18.3	18.8	18.7	16.3	17.2	17.7	16.5
C_3	14.3	16.9	13.2	11.1	12.8	12.4	13.9	14.0	13.4	15.1
C_4	7.4	10.0	7.2	5.3	6.0	6.1	7.5	7.5	7.4	9.2
C_5	3.4	5.9	3.7	1.5	2.9	2.9	3.1	5.4	4.6	6.0
C_6	0.7	1.2	1.0	0.5	0.7	0.7	0.7	1.6	1.3	1.7
C_7	0.2	0.2	0.0	0.2	0.3	0.2	0.2	0.5	0.4	0.5
Aromatics	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Sulfide	2.9	2.6	1.7	10.9	12.5	12.5	21.9	13.6	12.8	16.7
Coke	21.3	16.0	19.0	30.7	29.1	27.7	23.6	26.9	29.2	32.7
% Carbon	90.1	89.3	90.9	86.4		85.9		83.5		86.6
% Nitrogen	1.37	1.33	1.35	1.45		1.46		1.46		1.64
% Sulfur	2.09	2.18	2.09	5.80		6.01		6.76		6.93
Fractionation, wt%										
IBP-190°C	13.0	11.9	15.6	14.0	14.1*		20.3*		14.1*	
190-290°C	20.3	18.9	24.7	22.9	27.2		31.7		21.4	
290-360°C	23.9	23.0	30.5	23.3	24.4		27.8		22.4	
360°C+	42.3	44.9	28.5	38.0	38.6		19.8		41.5	

* In order to assure sufficient amounts of the liquid product for further tests, liquid effluents from two runs under the same conditions were combined. Cracked Liquids from 510°C Lloydminster Combined; Cracked Liquids from 490 and 510°C Athabasca Combined.

TABLE 3

COKING WITH STEAM INJECTION

	I.P.L.	Lloydminster	Lloydminster	Lloydminster	Athabasca
Coking Temperature, °C	510	510	510	510	510
Steam Injection Rate g/min	0.19	0.19	0.30	0.06	0.07
Reactor Charge Wt. (g)	198.0	146.8	136.3	139.2	150.2
% Light Oils	62.2	60.9	58.8	59.6	40.3*
% Coke	12.6	20.8	25.7	14.9	-
% Uncracked VTB	20.8	6.1	5.6	16.0	-
Gases, volume w/w %	3.6	5.6	7.2	6.8	-
Physical Properties; Oils					
Gravity	0.9243	0.9094	-	0.8835	0.8713
Viscosity 40°C, cSt	4.84	8.44	-	4.21	1.28
Total Sulfur, wt%	0.64	3.90	-	3.58	3.26
Total Nitrogen, ppm	1470	1235	-	1309	1201
Fractionation Light Oils	61.8**	60.9	58.8	53.7	40.3
IBP-190°C wt%	9.6	10.6	8.1	9.3	-
190-290°C wt%	6.6	19.1	12.9	20.3	-
290-360°C wt%	12.1	16.5	9.9	22.4	
360°C+ wt%	71.7	53.5	68.1	47.5	-

* Lost sample - inconclusive results

** Water/oil emulsion resulted in some losses of the light end on distillation.

TABLE 4

RESIDUUM CRACKING WITH IRON ORE AND SLAG

VTB	Lloydminster	Lloydminster	Athabasca	Athabasca
Charge wt. (g)	159.6	164.1	156.0	151.8
Cracking Temp., °C.	510	510	510	510
VTB/Solids Ratio	3/1	3/1	3/1	3/1
Solids Added	Slag	Iron Ore	Slag	Iron Ore
Light Oils, w/w %	45.3	55.6	37.7	54.1
Coke, wt. %	126.0	23.9	27.5	22.4
Residual VTB, wt.%	11.6	6.2	10.2	6.9
Gases, w/w %	12.9	9.2	21.8	10.9
Material Balance	95.8	94.9	97.2	94.3
Physical Properties: Oils				
Gravity	0.8489	0.8612	0.8505	0.8930
Viscosity 40°C cSt	1.91	2.39	2.54	3.95
Total Sulfur wt.%	2.61	2.86	2.65	3.31
Total Nitrogen ppm	711	1030	714	1585

TABLE 5

RESIDUUM CRACKING IN THE PRESENCE OF SAND

VTB	Lloydminster	Lloydminster	Athabasca	Athabasca
VTB/Sand Ratio	6:1	3:1	6:1	3:1
Charge wt. VTB (g)	155.0	156.5	159.1	149.0
Coking Temp., °C	510	510	510	510
Light Oils, w/w %	61.7	63.3	42.1	43.3
Coke, w/w %	18.4	6.79	19.0	29.3
Residual VTB, w/w %	5.0	18.1	19.0	10.4
Gases, w/w %	12.8	11.5	7.8	10.7
	97.9	99.6	89.9	93.7
Physical Properties: Oils				
Gravity	0.8511	0.9072	0.8621	0.8422
Viscosity 40°C cSt	1.95	9.39	2.94	1.58
Total Sulfur wt.%	2.39	3.11	3.16	2.67
Total Nitrogen ppm	605	909	1193	887
Fractionation				
IBP-190°C	18.5	6.8		
190-290°C	35.1	15.7		
290-360°C	27.2	14.7		
360°C+	18.2	38.7		

TABLE 6

COKING TESTS - REPETITIONS AND MODEL FEEDS

VTB	Conditions	Temperature	% Oil	% Entrained VTB & % Coke	% Gases*	Overhead Heavy End (VTB)
Lloydminster	Reference Run	510°C	58.0	22.1	16.9	-
Lloydminster	Sand 3/1	510°C	52.6	31.1	16.3	-
Lloydminster	Sand 3/1	510°C	56.6	29.1	14.3	-
Lloydminster	Steam 0.30 g/m	510°C	61.1	24.6	14.3	-
Athabasca	Sand 3/1	510°C	53.0	30.6	16.4	-
I.P.L.	Reference Run	510°C	63.3	21.1	15.6	-
I.P.L.	Steam 0.19 g/m	510°C	57.1	23.3	19.0	-
I.P.L./Metals 143.3 g/0.0814 g	Nickel(II)Tetraphenylporphine Added	510°C	59.7	26.8	13.5	-
I.P.L./Metals 103.18 g/0.1420 g	Vanadium(IV)Tetraphenylporphine Added	510°C	64.4**	11.0	16.1	8.5
I.P.L./Metals 101.224 g/Ni 0.0102 g V 0.2837 g	Nickel and Vanadium Tetraphenyl-porphines Added	510°C	59.6	10.8	17.5	12.1

* Contains purging nitrogen

** Heavy ends, uncracked material carried over

TABLE 7

MICRO SCALE COKING TESTS

VTB	Run No.	Addition (g/min) rate	Charge (g)	Liquids (g)	% Liquids	Gas Vol. (L)	Coker Gas (L)	Wt% Gas	Weight Coke (g)	% Coke	Mass Balance
I.P.L.	1	0.1350	2.3404	1.2490	53.37	0.68	0.37	15.5	0.4611	19.70	88.57
I.P.L.	2	0.1350	2.5171	1.3656	54.25	0.59	0.40	20.5	0.4083	16.22	98.97
I.P.L.	3	0.1350	2.1852	1.2937	59.20	0.50	0.28	16.5	0.4493	20.56	96.26
I.P.L.*	4a	0.1220	5.3866	3.5996	65.67	0.60	0.39	9.43	)		91.86
									)1.8641	16.86	
	4b	0.1220	5.6705	3.4918	61.589	0.86	0.60	13.60	)		92.04
I.P.L.	5	0.1080	5.1182	3.1954	62.43	1.02	0.59	16.02	0.6616	12.93	91.38
Lloydminster	6	0.1350	4.2020	2.4097	59.72	0.56	0.32	10.35	1.1502	27.37	97.44
Lloydminster	7	0.1350	5.3899	3.0485	56.55	0.98	0.51	12.13	1.5172	28.15	96.83
Lloydminster	8	0.1220	6.6962	3.6767	54.91	0.91	0.52	9.75	2.0251	30.34	95.00

* Two successive injections

TOTAL 8

BOILING POINT DISTRIBUTION IN TOTAL LIQUID PRODUCT, T°C
COKING TESTS AT 510°C

% OFF	IPL VTB		LLOYDMINSTER VTB	
	Macro Test	Micro Test #5	Macro Test	Micro Test #7
IBP	41	46	32	33
10	121	121	120	116
20	168	186	171	167
30	209	246	221	211
40	245	303	264	249
50	277	362	302	283
60	307	414	340	316
70	338	467	375	350
80	368	515	419	386
90	412	557	478	436
FBP	531	630	570	550

TABLE 9

PRODUCT INSPECTIONS
(MACROSCALE REFERENCE RUNS)

VTB	I.P.L.	I.P.L.	Lloydminster	Lloydminster	Athabasca	Athabasca
Coking Temperature, °C	460	510	460	510	490	510
Bromine No.						
IBP-190°C	44.7	47.4	49.3	-	56.7	59.4
190-290°C	32.6	30.9	44.7	51.6	52.0	62.3
290-360°C	14.4	14.1	26.7	19.3	16.3	22.3
360°C+	-	-	-	-	-	-
Specific Gravity						
IBP-190°C	0.7552	0.7351	0.7507	0.8384	0.7632	0.7523
190-290°C	0.8217	0.8179	0.8403	0.8946	0.8446	0.8452
290-360°C	0.8660	0.8617	0.8979	0.9424	0.9044	0.9042
360°C+	0.8909	0.8975			0.9481	0.9548
Total Sulfur Content w/w %						
IBP-190°C	7.6	0.3	1.99	-	7.9	2.3
190-290°C	2.0	0.4	3.05	2.95	3.5	3.3
290-360°C	0.6	0.6	3.76	2.84	4.4	4.2
360°C+	0.7	0.7		2.72	3.90	3.2
Total Nitrogen ppm						
IBP-190°C	115	55	83.4	lost	172	126
190-290°C	378	333	375	395	502	478
290-360°C	1015	918	781	954	1318	1184
360°C+	2069	2049		2146	2532	2701

TABLE 10

PRODUCT INSPECTIONS - CRACKING LLOYDMINSTER VTB WITH SAND OR STEAM

Boiling Range	IBP-190	190-290	290-360	360°C+
Ratio of Crude/Sand (3/1)				
Bromine No.	52.3	38.8	19.2	--
Gravity	0.7505	0.8384	0.8972	--
Sulfur, %	3.09	3.08	3.38	--
Nitrogen, ppm	580	250	640	--
Ratio of Crude/Sand (6/1)				
Bromine No.	--	34.3	14.2	--
Gravity	--	0.8417	0.8973	--
Sulfur, %	--	2.85	--	--
Nitrogen, ppm	--	280	690	--
Steam Injection Rate (0.19 g/min)				
Gravity	--	0.8481	0.8959	
Bromine No.	42.2	34.1	20.7	
Sulfur, %	--	2.97	3.47	
Nitrogen, ppm	--	210	810	

TABLE 11

PRODUCT INSPECTIONS (MACROSCALE RUNS)

(See Table 6 for Operating Conditions and Yields)

VTB	LL	LL	LL	LL	A	IPL	IPL	IPL	IPL	IPL
Test Type, °C	Ref.	Sand	Sand	Steam	Sand	Steam	Ref.	Ni Add.	V Add.	Ni,V Add.
Bromine No.										
IBP-190°C	53.9	55.2	50.7	45.1	49.2	52.2	53.9	57.8	45.3	51.5
190-290°C	46.4	46.5	40.5	34.0	46.6	38.8	46.4	35.3	43.6	36.2
290-360°C	27.5	12.0	23.7	27.8	32.9	25.8	27.5	22.8	28.1	26.0
Specific Gravity										
IBP-190°C	0.7559	0.7777	0.7670	0.8035	0.7777	0.7617	0.7597	0.7515	0.7656	0.7608
190-290°C	0.8373	0.8517	0.8465	0.8691	0.8538	0.8300	0.8297	0.8313	0.8150	0.8432
290-360°C	0.8925	0.9013	0.8943	0.8976	0.9046	0.8987	0.8833	0.8788	0.8710	0.8680
360°C+	0.9452	0.9535	0.9395	0.9701	0.9628	0.9253	0.9279	0.91180	0.9635	0.9328
Total Sulfur Content w/w %										
IBP-190°C	1.34	2.22	1.49	1.86	2.44	0.57	0.97	0.50	0.68	0.65
190-290°C	2.21	2.85	2.25	2.69	3.18	0.83	0.93	0.82	0.75	1.23
290-360°C	2.89	3.36	2.80	2.98	3.89	1.34	1.38	1.28	1.32	1.19
360°C+	2.88	3.32	2.65	3.05	3.84	1.29	1.26	1.19	1.55	1.22
Total Nitrogen ppm										
IBP-190°C	68.7	97.3	112	197	127	66.3	74.9	74.9	25.6	54.2
190-290°C	312	507	462	539	522	315	288	416	310	178
290-360°C	893	1051	924	877	1095	862	877	971	884	703
360°C+	1918	2366	1759	2364	2113	1983	2111	2011	2002	1559
Fractionation, wt%										
IBP-190°C	11.2	15.5	17.1	6.7	19.2	10.9	12.5	12.2	4.0	9.9
190-290°C	20.2	27.0	23.2	12.8	21.3	16.3	17.6	22.5	7.5	17.9
290-360°C	21.1	23.7	22.6	15.0	19.5	18.4	20.8	19.1	11.1	18.0
360°C+	47.0	32.2	36.1	64.2	38.9	54.3	49.0	45.8	76.8	53.3

TABLE 12

DISTRIBUTION OF HYDROCARBON TYPES IN NAPHTHAS, VOL%

Z No.	Hydrocarbon Type	I.P.L. (460°C)	I.P.L. (510°C)	Lloydminster (460°C)	Lloydminster (510°C)	Athabasca (510°C)	I.P.L. (510°C) 0.19 g/min H_2O	I.P.L. (510°C) 0.30 g/min H_2O	Lloydminster (510°C) 0.19 g/min H_2O	Lloydminster (510°C) 0.30 g/min H_2O
+ 2	Paraffins	42.7	37.3	40.6	39.2	39.7	37.7	39.4	39.5	37.7
0	Monocycloparaffins	18.8	21.3	12.9	15.4	13.1	20.6	27.1	18.0	22.8
- 2	Dicycloparaffins	3.0	2.1	2.7	3.8	2.1	4.6	6.6	2.4	10.0
- 4	Tricycloparaffins	0.9	1.8	1.4	1.0	1.6	2.0	5.4	1.2	3.5
0	Monoolefins	15.7	15.0	23.7	21.3	23.9	14.0	6.6	20.8	11.9
- 2	Cycloolefins	14.5	15.0	14.3	15.3	15.3	15.6	9.3	14.7	9.3
- 4	Dicycloolefins	0.6	0.8	0.5	1.1	0.8	1.0	0.2	0.9	0.7
- 6	Alkylbenzenes	3.1	5.2	3.2	2.4	2.9	4.0	4.6	2.3	3.8
- 8	Styrene/Indans	0.4	0.2	0.3	0.2	0.2	0.2	0.5	0.0	0.3
-10	Indenes	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.2
-12	Naphthalenes	0.1	0.1	0.1	0.1	0.3	0.1	0.1	0.0	0.1
-14	Biphenyls	0.1	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.1

TABLE 13

DISTRIBUTION OF HYDROCARBON TYPES IN NAPHTHAS FROM VTBS CRACKED WITH SAND IN RATIO 3:1, VOL%

Z No.	Hydrocarbons	Reference Runs		Sand Added		
		Lloydminster 510°C	Athabasca 510°C	Lloydminster Run 1	Lloydminster Run 2	Athabasca
+ 2	Paraffins	38.6	39.7	38.7	38.8	39.1
0	Monocycloparaffins	15.8	15.4	17.5	17.2	13.7
- 2	Dicycloparaffins	5.1	3.8	3.1	2.8	4.4
- 4	Tricycloparaffins	1.9	1.0	1.8	1.5	2.1
0	Monoolefins	20.2	21.3	19.1	20.2	21.8
- 2	Cycloolefins	13.9	15.3	14.8	14.7	14.0
- 4	Dicycloolefins	0.9	0.8	0.8	1.0	0.6
- 6	Alkylbenzenes	3.2	2.9	3.9	3.5	3.7
- 8	Styrene/Indans	0.2	0.2	0.2	0.2	0.2
-10	Indenes	0.1	0.1	0.1	0.1	0.2
-12	Naphthalenes	0.1	0.3	0.0	0.0	0.1
-14	Biphenyls	0.0	0.0	0.0	0.0	0.0

TABLE 14

DISTRIBUTION OF HYDROCARBON TYPES IN DISTILLATES AND GAS OILS BY MASS SPECTROMETRY, MASS %

Hydrocarbons	IPL/510°C			REFERENCE RUNS Lloydminster/510°C*(460°C)			Athabasca 510°C		
	190-290	290-360	360°C*	190-290	290-360	360°C+	190-290	290-360	360°C+
Paraffins	36.9	29.4	19.4	28.6(28.8)	18.0(17.7)	8.6(10.0)	26.6	15.1	7.0
Cycloparaffins	44.4	43.5	37.9	49.3(49.2)	42.1(42.7)	31.0(33.4)	50.1	42.1	28.8
Monoaromatics	16.4	15.9	16.0	18.9(18.6)	20.7(20.1)	15.5(16.8)	19.4	21.1	16.1
Diaromatics	2.2	7.3	11.7	2.0(2.0)	9.7(8.9)	13.2(13.5)	2.1	10.0	14.6
Triaromatics	0.0	1.1	6.6	0.0(0.0)	1.0(1.0)	7.6(7.5)	0.0	1.0	9.4
Tetraaromatics	0.0	0.4	2.5	0.0(0.1)	0.6(0.7)	3.6(3.2)	0.1	0.6	4.4
Pentaaromatics	0.0	0.0	0.8	0.0(0.0)	0.0(0.0)	2.8(1.3)	0.0	0.0	3.2
Polyaromatics	0.0	0.0	0.0	0.0(0.0)	0.0(0.0)	0.1(0.0)	0.0	0.0	0.3
Thiophenes	0.1	2.5	4.8	1.3(1.3)	8.4(9.0)	17.4(14.0)	1.8	10.1	16.2
Furans	0.0	0.0	0.1	0.0(0.0)	0.0(0.0)	0.2(0.1)	0.0	0.0	0.0

* Analyses in duplicate for all three fractions of the Lloydminster VTB cracked at 510°C. Similar results of the compositional analyses performed in March and May indicate the stability of both fractions.

TABLE 15

DISTRIBUTION OF HYDROCARBON TYPES IN DISTILLATES AND GAS OILS
BY MASS SPECTROMETRY, MASS %
STEAM INJECTION TESTS

	LLOYDMINSTER									I.P.L.		
	190-290°C			290-360°C			360°C+					
Hydrocarbons	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	190-290	290-360	360°C+
Paraffins	29.0	29.1	28.1	15.5	16.1	15.9	10.1	9.6	11.0	31.4(32.1)*	26.2(24.0)	17.8
Cycloparaffins	51.0	50.7	51.8	45.7	44.7	44.0	33.9	38.3	37.0	47.5(48.4)	48.1(50.2)	44.2
Monoaromatics	17.0	17.3	17.4	20.6	20.4	20.3	15.4	20.4	16.0	16.7(17.1)	15.5(16.7)	18.0
Diaromatics	1.7	1.7	1.7	8.6	8.8	8.9	11.5	10.3	10.0	3.4(1.9)	6.4(5.2)	9.4
Triaromatics	0.0	0.0	0.0	0.8	0.7	1.2	6.8	5.2	6.4	0.0(0.0)	1.4(0.1)	5.2
Tetraaromatics	0.0	0.1	0.0	0.5	0.6	0.7	3.8	1.4	3.2	0.0(0.0)	0.3(0.4)	1.5
Pentaaromatics	0.0	0.0	0.0	0.0	0.0	0.0	1.9	1.5	1.8	0.0(0.0)	0.0(0.0)	0.9
Polyaromatics	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0(0.0)	0.0(0.0)	0.0
Thiophenes	1.1	1.1	0.9	8.3	8.8	9.1	16.3	13.5	14.4	0.9(0.4)	2.1(3.4)	3.0
Furans	-	-	-	-	-	-	0.2	0.2	0.3	-	-	-

* Duplicate runs at 0.19 g/min in brackets.

TABLE 16

DISTRIBUTION OF HYDROCARBON TYPES IN DISTILLATES AND GAS OILS BY MASS SPECTROMETRY, MASS %
COKING WITH SAND

L L O Y D M I N S T E R

Hydrocarbons	Ratio 3:1			Ratio 6:1		
	190-290	290-360	360°C+	190-290	290-360	360°C+
Paraffins	27.5(27.4)*	16.0(18.4)*	11.6	26.4	17.2	13.1
Cycloparaffins	51.2(48.1)	41.9(41.4)	38.0	49.4	40.4	35.6
Monoaromatics	18.3(20.0)	21.5(20.0)	14.7	19.9	20.4	15.9
Diaromatics	1.8(2.5)	10.1(9.9)	12.0	2.5	11.0	10.4
Triaromatics	0.0(0.0)	1.6(0.0)	7.5	0.0	2.0	8.2
Tetraaromatics	0.0(0.1)	0.5(0.6)	2.9	0.0	0.9	3.0
Pentaaromatics	0.0(0.0)	0.0(0.2)	1.8	0.0	0.0	2.7
Polyaromatics	0.0(0.0)	0.0(0.0)	0.0	0.0	0.0	0.0
Thiophenes	1.1(1.9)	8.3(9.7)	10.2	1.7	8.2	10.9
Furans	-	-	0.4	-	-	0.2

* Duplicate runs ()

TABLE 17

COKE COMBUSTION PROFILES BY TGA, T °C

Feed	Test	T_o	T_{xo}	T_i	T_c	T_{25}	T_{50}	T_{75}
LL	Ref. Run at 510°C	360	440	470	570	471	509	557
LL	Duplicate Run at 510°C	349	457	490	521	484	500	515
LL	Coking at 460°C	350	440	460	540	457	470	515
LL	Microscale Coking	350	454	489	521	480	497	512
LL	Steam Injection	327	387	417	434	416	429	446
IPL	Ref. Run at 510°C	350	460	500	540	485	507	525
IPL	Duplicate Run at 510°C	360	466	504	536	498	515	529
IPL	Coking at 460°C	340	460	500	540	477	507	525
IPL	Microscale Coking	330	460	493	515	488	502	511
IPL	Steam Injection	349	450	481	510	478	492	505
IPL	Ni Porphine Addition	362	462	493	515	488	502	511
A	Ref. Run at 510°C	350	450	480	550	469	486	515
A	Coking at 490°C	340	420	440	520	434	450	472

TABLE 18

COKE VOLATILE RELEASE PROFILES BY TGA, W/W%

Feed	Test	Moisture	Volatiles	Fixed Carbon	Ash
LL	Coking at 460°C	1.00	15.38	81.82	1.56
LL	Coking at 510°C	0.70	9.08	87.29	2.63
LL	Duplicate Run at 510°C	1.03	1.27+5.99	87.93	3.60
LL	Microscale Coking	0.97	3.04	96.79	5.39
LL	Steam Injection	0.91	0.55+14.53	82.02	1.97
A	Coking at 510°C	0.76	11.93	84.76	3.07
A	Coking at 490°C	3.71	28.15	64.84	3.19
IPL	Coking at 460°C	1.95	16.00	81.59	0.46
IPL	Coking at 510°C	2.68	15.03	81.93	0.41
IPL	Microscale Coking	0.32	6.41+4.96	86.36	2.01
IPL	Duplicate Run at 510°C	1.93	2.00+4.16	90.51	1.27
IPL	Ni Porphine Addition	2.75	1.46+4.52	90.4	0.78
IPL	Steam Injection	2.34	0.59+9.33	86.87	0.76

TABLE 19

SEMI-QUANTITATIVE ANALYSIS OF COKE BY SCANNING ELECTRON MICROSCOPY, WT%

Feed	Test	Contents Normalized to 100%*	Comments
IPL	Ref. Run at 510°C	Si - 6.4; S - 93.6	
IPL	Coking at 460°C	Si - 7.2; S - 92.8	
IPL	Steam Injection	Si - 4.9; S - 95.1	
IPL	Microscale Test	Si - <0.1; S - 64.0 Fe - 12.8; Cl - 23.1	Further investigation indicated the presence of Cl as KCl; Cl - even distribution; Fe - concentrated areas and particles scattered throughout sample.
LL	Ref. Run at 510°C	S - 77.9; Si - <0.1 Cl - 22.1	Increased magnification revealed the Cl to be in the form of NaCl; Cl - concentrated areas scattered throughout sample.
LL	Coking at 460°C	Si - 5.7; S - 94.3	
LL	Steam Injection	Si - 6.3; S - 93.7	
A	Ref. Run at 510°C	Si - 8.3; S - 91.7	
A	Coking at 490°C	Si - 9.8; S - 82.0 Fe - 8.1; Al - <0.1	Fe and Al - evenly distributed throughout sample
A	Steam Injection	Si - 9.8; S - 80.7 V - 2.1; Fe - 5.4 Al - 2.5	Al and V - evenly distributed throughout sample, Fe - two hot spots (area of higher concentreation) detected.

* Normalization excludes elements which are not determined such as C, H, O.

LIST OF FIGURES

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2. MICROSCALE COKING APPARATUS

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4. INSPECTION OF LIGHT DISTILLATES FOR COMPOUND TYPES

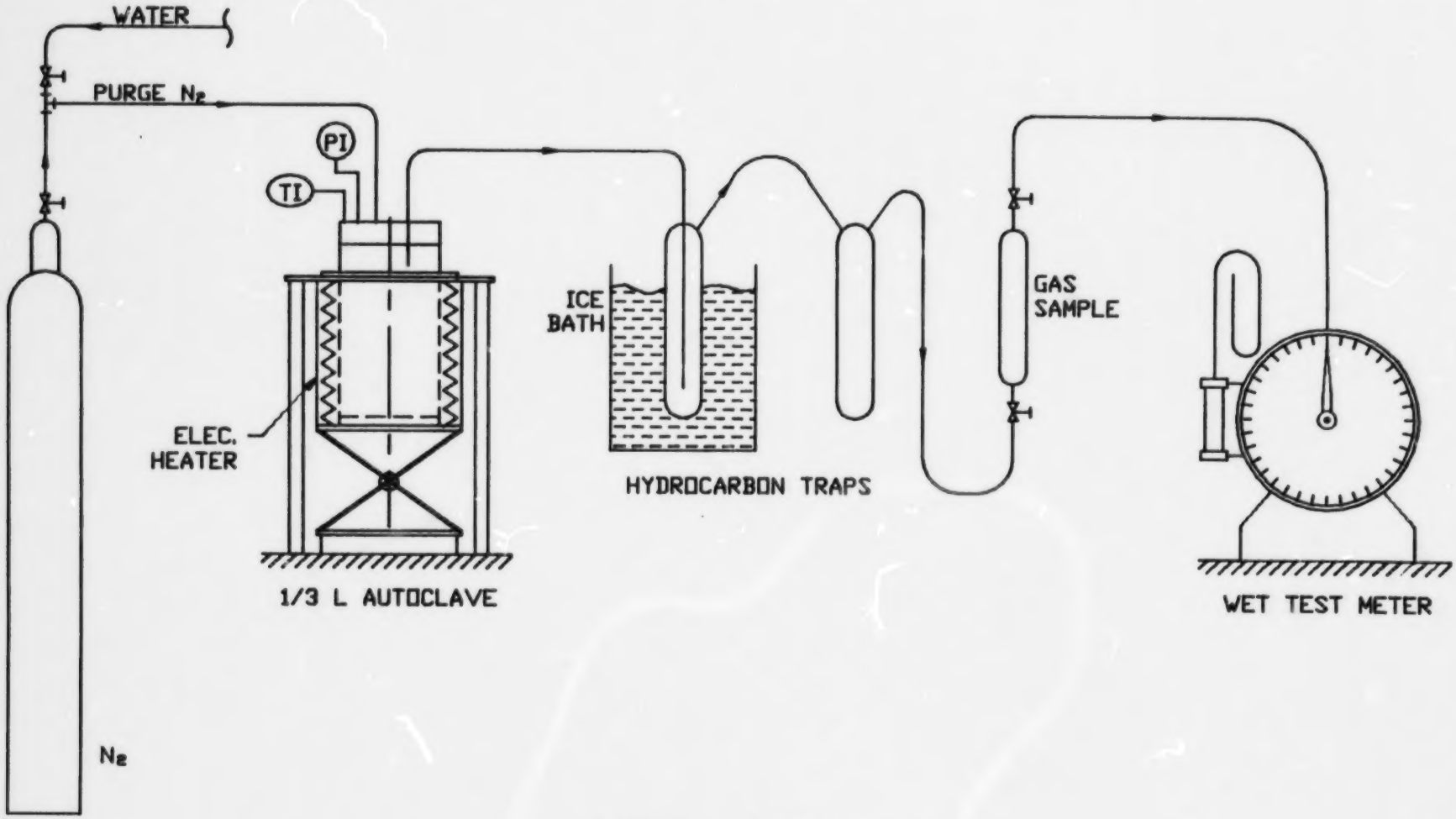
5. INSPECTION OF HEAVY DISTILLATES FOR COMPOUND TYPES

6. INSPECTION OF GAS OILS FOR COMPOUND TYPES

7 EXAMINATION OF COKE SAMPLE BY SEM

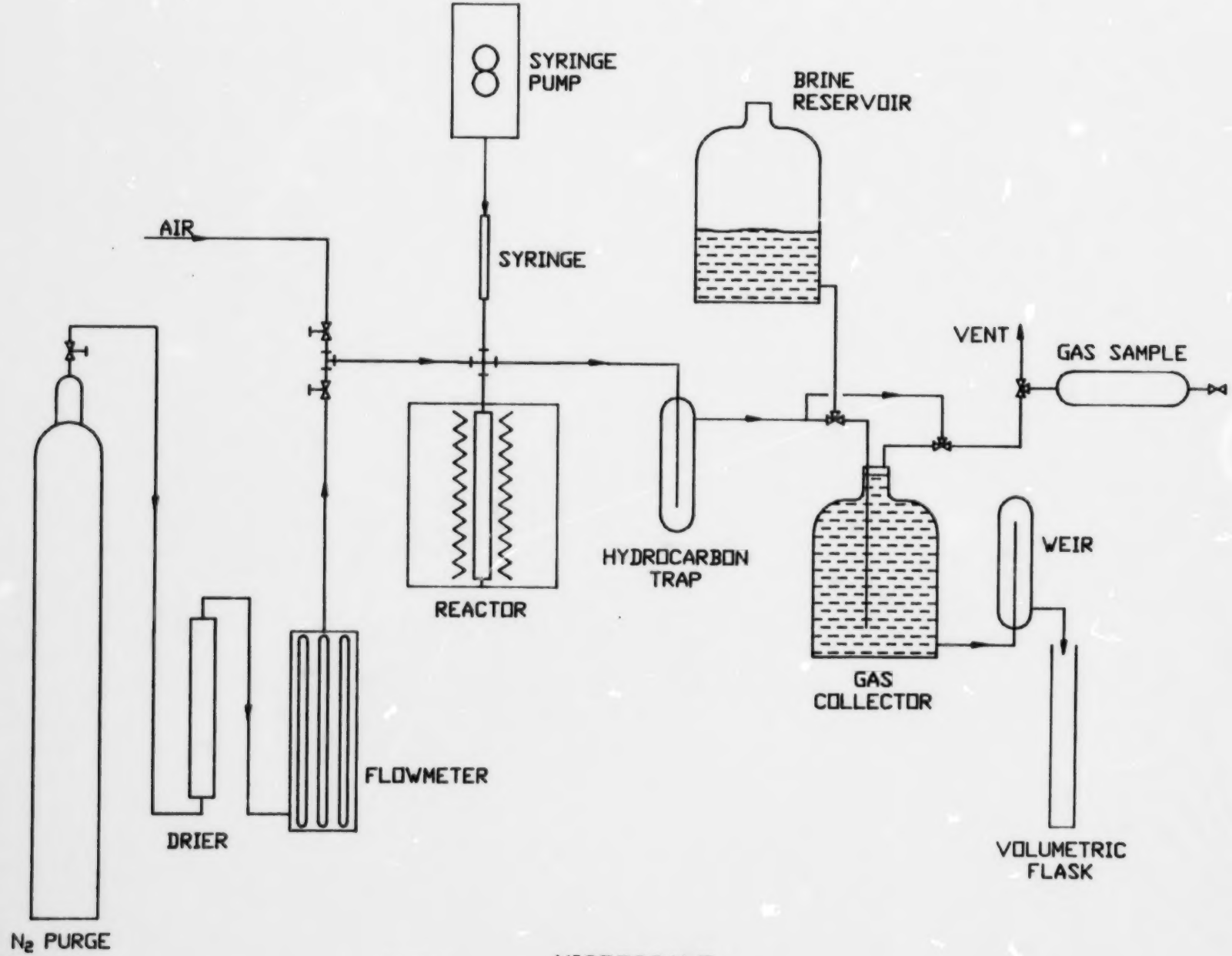
A. TYPICAL SURFACE (IPL VTB AT 510°C)

B. GRANULAR TYPE (ATHABASCA BITUMEN VTB AT 490°C)



COKING APPARATUS

FIGURE 1



MICROSCALE
COKING APPARATUS

FIGURE 2

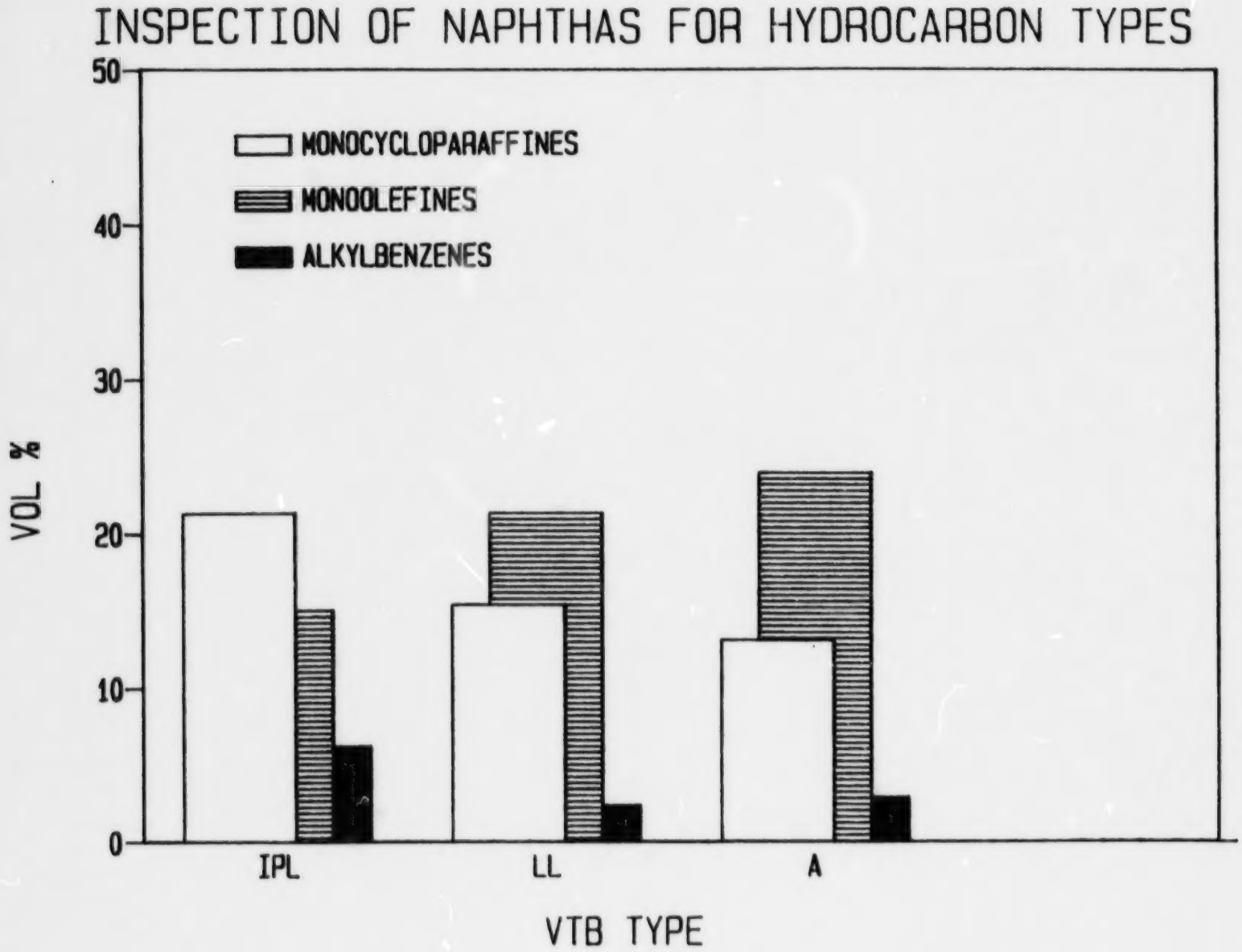

INSPECTION OF NAPHTHAS FOR HYDROCARBON TYPES
MONOCYCLOPARAFFINES
MONOOLEFINES
ALKYLBENZENES
VOL %
50
40
30
20
10
0
IPL
LL
A
VTB TYPE

FIGURE 3

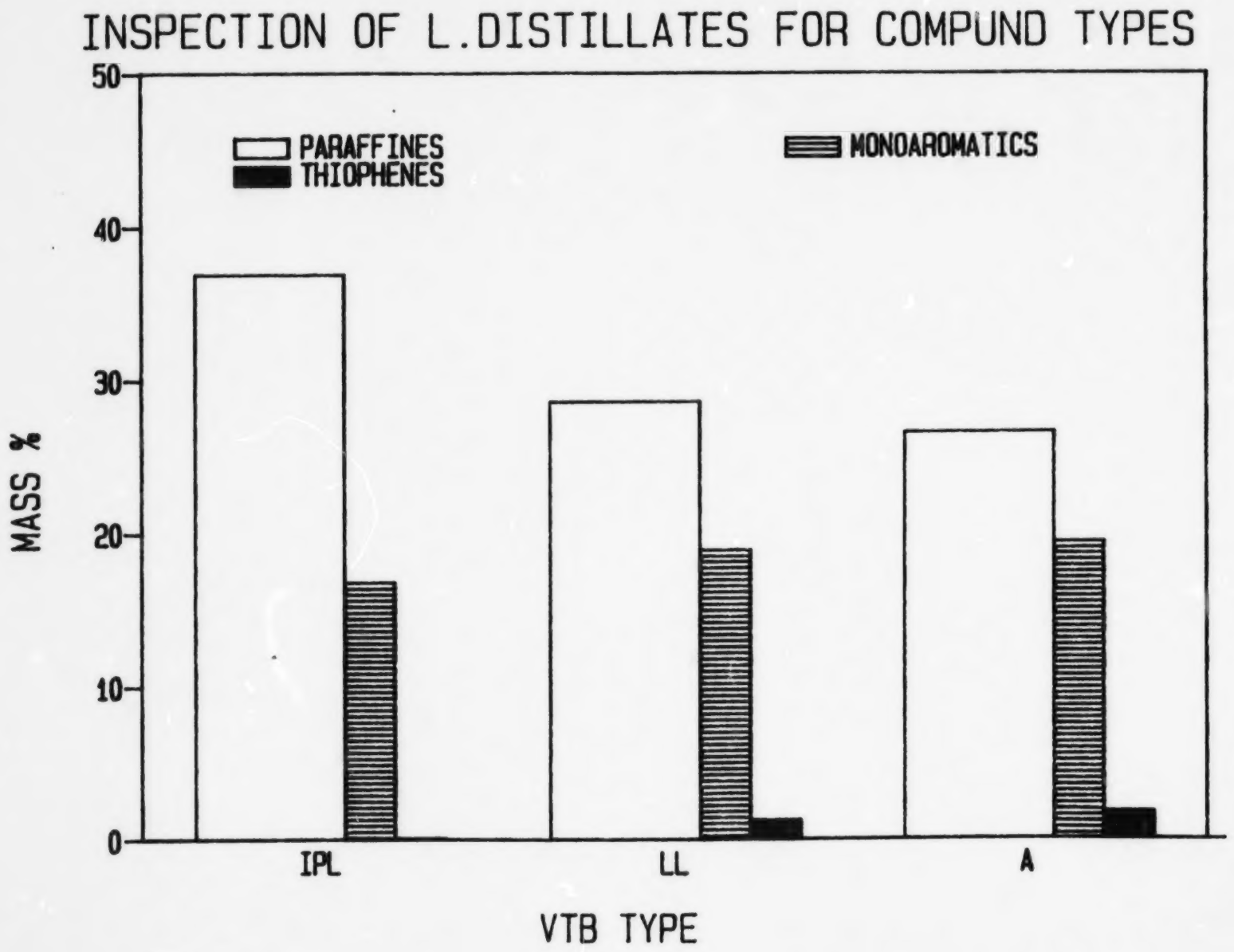

INSPECTION OF L.DISTILLATES FOR COMPUND TYPES
50
40
30
20
10
0
MASS %
PARAFFINES
THIOPHENES
MONOAROMATICS
IPL
LL
A
VTB TYPE

FIGURE 4

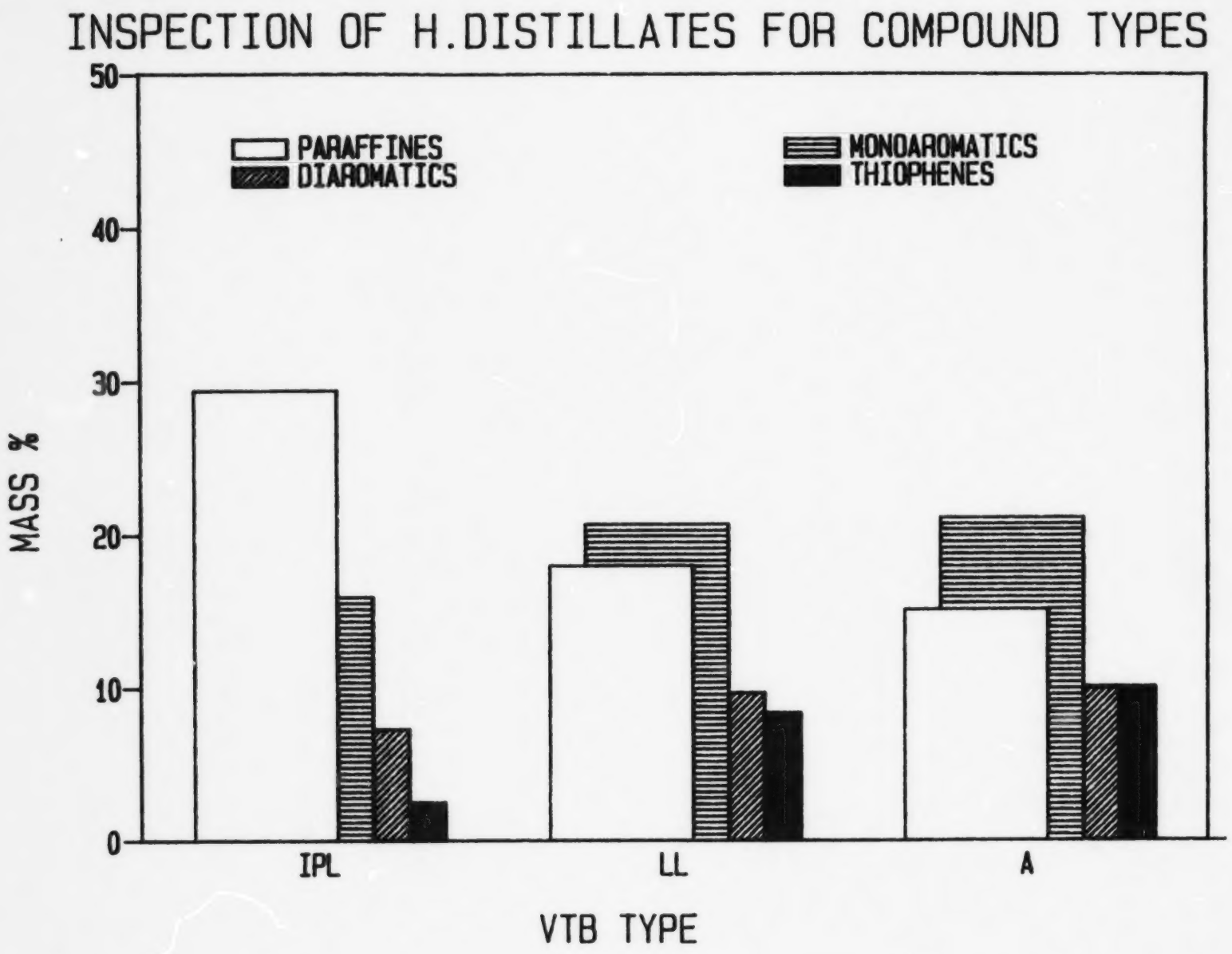

INSPECTION OF H.DISTILLATES FOR COMPOUND TYPES
PARAFFINES
DIAROMATICS
MONOAROMATICS
THIOPHENES
MASS %
50
40
30
20
10
0
IPL
LL
A
VTB TYPE

FIGURE 5

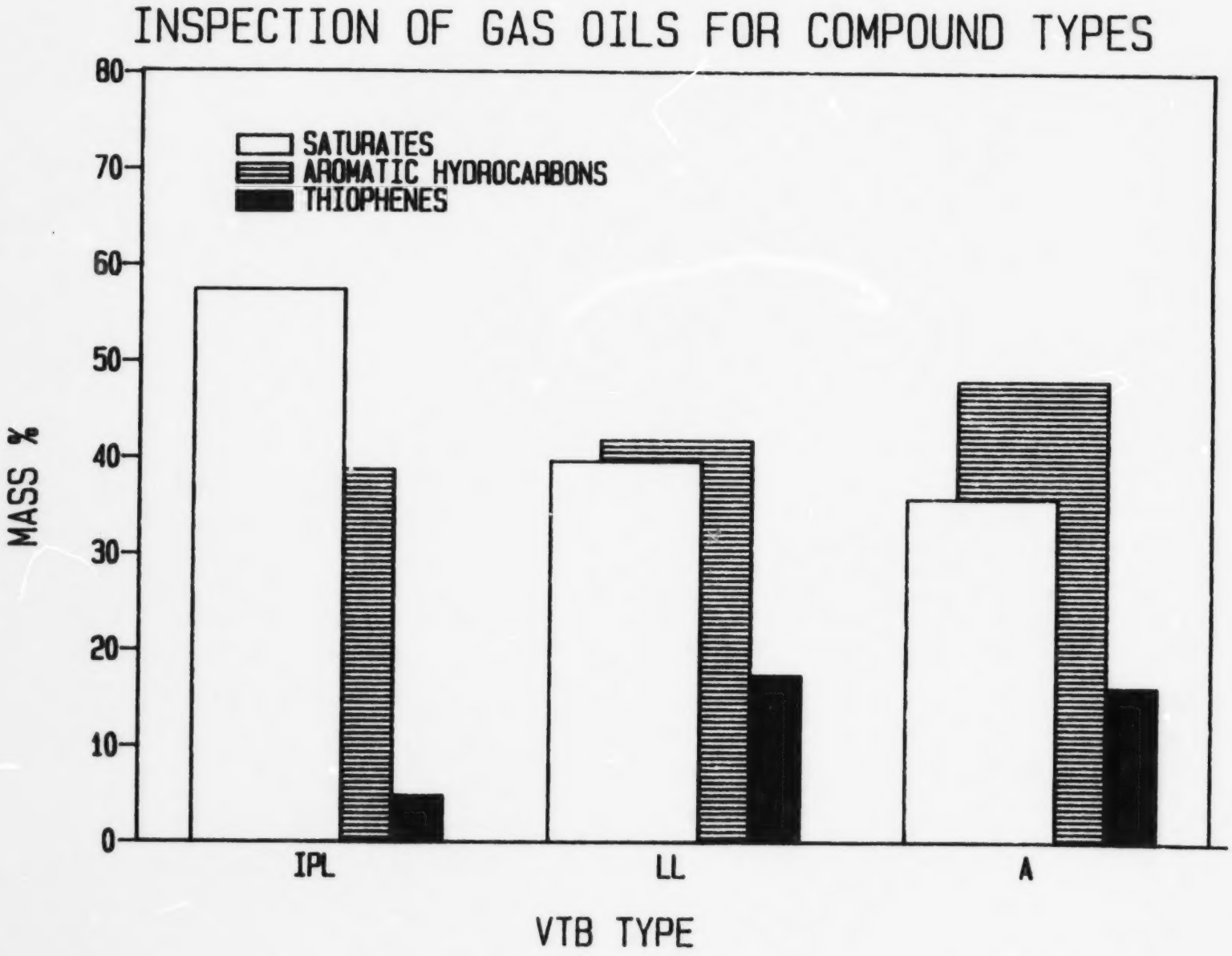
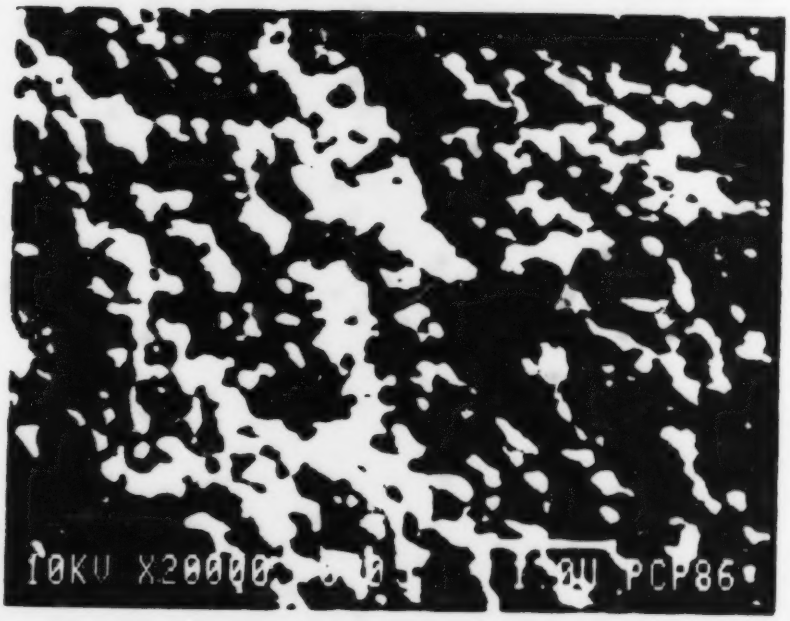

INSPECTION OF GAS OILS FOR COMPOUND TYPES
SATURATES
AROMATIC HYDROCARBONS
THIOPHENES
MASS %
80
70
60
50
40
30
20
10
0
IPL
LL
A
VTB TYPE

FIGURE 6

A



B

FIGURE 7